Interfacial tensions of fluid mixtures with polar and associating components

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ABSTRACT

In this contribution the gradient theory is applied for modelling the interfacial tensions of planar interfaces in multi component systems, in which one or more associating components are present. For this purpose, the square gradient theory is combined with the Associating-Perturbed-Anisotropic-Chain Theory. The results have been compared with results obtained with the gradient theory combined with the Peng-Robinson equation of state. The interfacial tensions computed from the new model agree very well with experiments for systems composed of normal alcohols and water. Even the interfacial tensions of a ternary system composed of water, hexane and ethanol can be described accurately. In order to improve the accuracy the influence parameter was a linear function of temperature.

Keywords: association, equation of state, interfacial tension, modelling, liquid-liquid equilibria, vapour-liquid equilibria.

INTRODUCTION

It is known that in several processes that are encountered in industry the interfacial tension plays a crucial role. For instance, processes encountered in the enhanced oil recovery and food industry. Therefore, it is intended to develop a tool that can be used to model and to predict this property. The model that has been selected is a combination of the gradient theory of van der Waals [1] and a modern engineering equation of state. This approach was introduced by Carey et al., [2], who used simple cubic equations like the Peng-Robinson equation of state [3]. Several authors have presented calculations with this model [2,4,5,6] and it appears that for non-polar species this approach gives good results. However, results for mixtures with associating components are poor, which is believed mainly to be due to an improper representation of the thermodynamic properties by the PREOS. Therefore, we intend to replace this equation by a model that incorporates association due to hydrogen bonding and anisotropic interactions. For that purpose, a suitable model is the Associated-Perturbed-Anisotropic-Chain Theory (APACT), developed by Donohue and co-workers [7,8]. In the present paper this APACT is incorporated into the gradient theory for modelling mixtures containing associating and polar species.

In the following section briefly the theory is introduced that has been applied in the present paper. Successively, the results that have been obtained with the new model will be presented and discussed. The last part of the paper lists the conclusions of the study.

THEORY

The model used for the modelling the interfacial tensions is the model introduced by Carey et al.[2]. This model combines the square gradient theory of van der Waals [1] with a modern engineering equation of state. The interfacial tension of a planar interface then reads:

$$\gamma = \int f(\) + \sum_{i,j=1} c_{i,j} \nabla_{i} \nabla_{j} - \sum_{i=1} \mu_{i_0 i} + p_0 dx$$
 (1)

, where the index 0 indicates thermodynamic equilibrium, ∇ represents d/dx, and c_{ij} is the so-called influence parameter that can be a function of both density and temperature, but is a linear function of temperature only in the present contribution (see also [9]). In this study the Helmholtz free energy density, f(), is modelled using APACT (or PREOS). For a complete description of the gradient theory and its connection to modern semi-empirical equations of state, one is referred to elsewhere [9,10]. All parameters used for this set of calculations have been taken from Cornelisse [9]. The value of the influence parameter c_{ij} of the unlike species are computed from c_{ij} =(1- $_{ij}$)($c_{ii}c_{jj}$)^{1/2}, where the mixing parameter $_{ij}$ is an adjustable parameter [9,11].

RESULTS

In this section the computed interfacial tensions of mixtures with associating components are presented by making use of the APACT. The results will be compared with those obtained with the PREOS. The first mixture that is examined is a system composed of water and ethanol. Fig. 1 shows the phase diagram at 313.15 K. It appears that the APACT gives much better results compared to the PREOS. Even the location of the azeotropic point is described accurately by APACT.

The interfacial tension of the mixture is plotted in two figures. In the first figure (Fig. 2) the interfacial tensions are shown at a temperature of 293.15 K. For the PREOS a good agreement between theory and experiment could not be attained. Apparently, the deviations in the description of the phase behaviour prevent this equation to yield accurate interfacial tensions. Therefore, it was decided to leave the results obtained with the PREOS out of the remaining discussion of the system under study.

In Fig. 2, for the APACT two (solid) lines have been added for two different values of the mixing parameter 12. The upper line is computed with a value of 0.0, while the lower line is computed with a value of 1.0. It is clear from this figure that with a value of 12=1.0 the experimental interfacial tensions are described very well by APACT. In addition, Fig. 2 shows that the sensitivity to changes in this parameter is not very large. It appears that as a first effect the interfacial tension increases upon an increase of the mixing parameter 12, while a further increase leads to a decrease of the interfacial tension. From a study of the interfacial concentration profiles it appears that the interfacial tension first rises upon an increase of the 12 parameter due to the fact that the accumulation of ethanol in the interface is reduced and the interface is broadened somewhat [9,11]. The effect of the withdrawal of the ethanol from the interface leads to higher tensions, while the broadening leads to lower tensions. Apparently, the first effect is stronger than the second one. A further increase of the 12 parameter yields broader interfaces and an even further reduction of the interfacial activity of ethanol. At these conditions the first phenomenon has a stronger effect and a lower interfacial tension is the result.

In Fig. 3 the computed excess interfacial tensions with the APACT are compared with experimental tensions [12] at three different temperatures. The excess tensions are computed as: $\gamma^E = \gamma - x_1 \gamma_1 - x_2 \gamma_2$. Again it is striking that the computations agree so well with the experiments, and that a good temperature dependence of the computed tensions is obtained.

Aside from the just described vapour-liquid interfacial tensions we will test our new model on the description of interfacial tensions of interfaces between two liquids. The system that has been selected for this purpose is a mixture composed of hexane and water. It has been discussed previously by [13] that it appears to be possible to describe the interfacial tensions at three-phase equilibrium liquid-liquid-vapour accurately. In the present paper the pressure dependence of the two-phase liquid-liquid interfacial tension is studied at five different temperatures, i.e., 298.15, 323.15 K, 373.15 K, 423.15 K, and 473.15 K. The results for the APACT and the PREOS are presented in Fig. 4. It is clear from this figure that the liquid-liquid interfacial tensions cannot be modelled accurately over a wide temperature and pressure range by means of the gradient theory in which the PREOS or APACT have been incorporated. The line computed with the APACT at a temperature of 298.15 K and at the three-phase pressure (=beginning of line at low pressure side) shows that an accurate description of the interfacial tension appears to be possible. However, this is achieved by optimization of the ₁₂ parameter for the description of interfacial tensions at three-phase equilibrium conditions, as was shown elsewhere [13]. If the pressure is increased up to extreme pressures, however, the experimental tensions denoted as the solid circles show hardly any pressure dependence, while the calculated tensions show a rather strong pressure dependence, which gives rise to very large errors at high pressures for all five temperatures. In addition, it is clear from Fig. 4 that also by increasing the temperature the deviations increase

between the computations obtained with the APACT and the experiments.

For the PREOS the pressure dependence of the interfacial tensions seems to be much closer to the experimental data. The temperature dependence, however, shows to be even worse than was found for the APACT. The observed deviation from experiments can partly be explained from a study of the density differences between the liquid phases, which is believed to be an important quantity in the computation of interfacial tensions. A more extensive discussion on this subject can be found elsewhere [9,11].

In the previous results the systems under study are binary mixtures. To test the predictive capabilities of the new model a ternary system is examined. For such system all parameters in the model have been fitted to pure component and binary data and thus the results obtained will be purely predictive. The system that has been selected is a system composed of hexane, ethanol, and water. The mixing parameters are: k_{we} =-0.10 (PR)/-0.01(APACT), k_{wh} =-0.10(PR)/0.0(APACT), and k_{eh} =0.01(PR)/-0.015(APACT); w=water, e=ethanol, and h=hexane [9]. The phase triangle that can be constructed for the ternary system is presented in Fig. 5. This figure shows the computations performed with the APACT, and the PREOS in comparison with experiment [14]. It must be noted that each tie line is actually the liquid-liquid equilibrium at three-phase equilibrium. Therefore, the pressure varies as one approaches the critical composition. The results obtained with the PREOS appear to be much more in error with the experiments than the results obtained with the APACT. The latter model predicts all compositions accurately except for the two experiments closest to the critical endpoint. In addition, it is clear that the critical point predicted by the APACT is more or less on the place where it should be located experimentally, while the PREOS gives a critical point far removed from this expected experimental critical point.

In Fig. 6 the interfacial tension results are shown that have been obtained with the gradient theory in conjunction with the APACT. The interfacial tensions of the three interfaces that are present at three-phase equilibrium are presented as a function of the mole fraction of hexane in the hexane-rich phase. The figure shows that the computations do agree rather well with the experimental tensions. Especially the agreement between the tension of the GL1 interface is very good. Also the sharp decrease of the interfacial tension between the water-rich and oil-rich phase upon addition of a small amount of ethanol is clear, although the experimental tensions show an even somewhat faster decrease.

The $_{ij}$ parameters are taken to be equal to the values obtained from calculations in binary systems, except for the parameter $_{eh}$. The reason for this is the following. If the parameters for computations with the APACT model are chosen to be equal to the values obtained from binary calculations, the matrix of influence parameters, c_{ij} , is no longer positive definite. However, the matrix needs to be positive definite for the numerical evaluation of the interfacial tensions [9,11]. Therefore, one of the mixing parameters needs to be adjusted. It is chosen to use $_{eh}$ for this purpose, which had a value of 0.01 for the computations in the binary mixture, because the interfacial tension appears to be rather insensitive to changes in this parameter. The value was adjusted with a small correction to assure that the matrix becomes positive definite. The value selected for the $_{eh}$ parameter amounts 0.15. The other parameters amount $_{we}$ =0.0, and $_{wh}$ =0.48.

The results obtained with the PREOS have not been included in the present paper because it appeared that the agreement between theory and experiment is rather poor. The main reason for this disagreement is the bad description of the phase equilibria by the PREOS of the selected system. For the interested reader a more complete discussion can be found elsewhere [9,11].

CONCLUSIONS

From the computations performed in the present contribution for several liquid mixtures composed of hydrocarbons and polar species, it is found that, introduction of the APACT in the gradient theory makes it possible to study more polar and associating species. As a general result,

it is found that in these kind of mixtures, typically composed of water and/or alcohols, the APACT is by far superior to the PREOS in describing the interfacial tensions. It appears that in these kind of systems the PREOS is not able to model correctly the experimental phase behaviour of very non-ideal species, which is reflected into the interfacial tension behaviour.

In addition, it is shown that the pressure dependence of the liquid-liquid interfacial tensions at constant temperature in a mixture composed of water and hexane, cannot be correctly described by both the APACT and the PREOS. It appears that these deviations partly are due to the incorrect description of the equilibrium densities and partly are due to an inappropriate description by the gradient theory. The latter is due to the fact that the gradient theory is strictly only valid for slowly varying densities, and thus when the densities vary rapidly when the pressure is raised, which is the case in the present system, the deviations will be more severe.

Finally, it has been encountered in the present work that the predictive value of the gradient theory in the description of ternary mixtures is limited. This is due to the fact that the matrix of influence parameters needs to be positive definite in order to allow a numerical evaluation of the interfacial tension.

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FIGURE CAPTIONS

- Fig. 1. Pressure-composition diagram for the binary system water/ethanol at 293.15 K. Solid line APACT; dashed line PREOS; solid circles experiments [15].
- Fig. 2. Interfacial tension-composition diagram for the liquid-vapour interface of the system water/ethanol at 293.15 K. Solid lines APACT; dashed line PREOS; solid circles experiments [12].
- Fig. 3. Excess interfacial tension-composition diagrams for the system water/ethanol at 323.15 K (upper), 308.15 K (middle), and 293.15 K (lower). Solid lines APACT ($_{12}$ =1.0); solid circles experiments at 323.15 K; open squares at 308.15 K; solid triangles at 293.15 K [12].
- Fig. 4. Liquid-liquid interfacial tensions of the system hexane/water at 298.15 K, 323.15 K, 373.15 K, 423.15 K, and 473.15 K. Solid lines APACT ($_{12}$ =0.53), dashed lines PREOS ($_{12}$ =0.48). Experiments: solid circles 298.15 K, open circles 323.15 K, solid squares

- 373.15 K, open squares 423.15 K, and solid triangles 473.15 K [16].
- Fig. 5. Liquid-liquid phase composition triangle at three-phase equilibrium of the system hexane/water/ethanol at 293.15 K. Solid curve APACT; dashed curve PREOS; open circles and tie lines experiments [14]; Solid circle critical point APACT; solid square critical point PREOS.
- Fig.6. Interfacial tensions at three-phase equilibrium of the system hexane/water/ethanol at 293.15 K. Solid curves APACT; experiments: solid circles GL2 interface, solid squares GL1 interface, solid triangles L1L2 interface [14].











